

On the Diffraction of Light by Particles Comparable with the Wave-length.

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This research was undertaken to investigate an effect first noticed by one of us (A. W. P.) when experimenting with the light scattered by suspensions of finely divided sulphur. These were obtained, in the well-known way, by depositing sulphur from a solution of thiosulphate of soda by means of a weak acid. When such a suspension is placed in the path of a beam from an arc lamp focussed on a screen, the image of the carbon is usually red, of greater or less depth according to the size and number of the diffracting particles. The production of this red colour has been satisfactorily explained by Lord Rayleigh* as due to the selective scattering of blue light by particles which are small compared with the wave-length of the light.

One of us noticed, however, that if time be given for the particles to increase in size (and possibly in number also) the solution after becoming nearly opaque becomes transparent again, but in this new stage an excess of *blue is transmitted*, which attains at one stage a deep indigo tint, this afterwards changing through various blue-green and green tints, to white.

This very remarkable result is in direct variance with the current theory of the action of small particles, and presents, therefore, a problem requiring investigation. While making quantitative measurements upon it we found that analogous phenomena had been observed previously, though no thorough investigation had been undertaken to explain the effect observed.

For example Captain Abney,† in connection with his preparation of a photographic plate which would be sensitive to the infra-red region, experimented with silver bromide and attempted to get it in a different molecular condition from that generally found. He says: "I need not detail the different methods of preparation of this compound in collodion that were carried out. In some cases I obtained it in a state which, when viewed by transmitted light, appeared of a sky-blue colour inclining to green, visibly absorbing the red. In this condition it (the photographic plate) was sensitive to the whole spectrum, visible and invisible."

* 'Phil. Mag.,' 1871, vol. 41, pp. 107-120, 274-279, 447-454 ; 1899, vol. 43, pp. 375-384.

† 'Phil. Trans.,' 1880, Pt. II, p. 653.

Again, Walther Ritz* gives a new method of preparing the sensitive compound, giving superior results to those obtained by Abney. In the course of his directions he notes:—"Les bromures de zinc et d'ammonium sont à peu près équivalents: on peut aussi remplacer le mélange d'alcool et d'éther par de l'alcool méthylique ou de l'acétone. La transformation du bromure d'argent est donc d'ordre purement physique; elle est d'ailleurs toujours accompagnée d'une augmentation du diamètre des grains. Enfin l'émulsion a été soumise sous pression à des températures allant jusqu'à 100° pendant une heure et 40° pendant 24 heures. Il n'a cependant pas été possible de dépasser la limite donnée par Abney, le bromure devenant granuleux et se décomposant La couleur caractéristique bleue de l'émulsion d'Abney (observée par transparence) apparaît ici immédiatement et à froid."

These observations made by others are important because they show that the phenomenon is not peculiar to sulphur.

Method of Investigation.

The research consisted of measuring, at various instants after setting free the thiosulphuric acid, the transparency of the suspension to monochromatic lights of various wave-lengths. For this purpose a Hüfner spectrophotometer was employed, designed and made by Messrs. Hilger and Co. Light passing first through a fixed nicol, and then through one which can be rotated, is matched with light passing through the solution and the second nicol. On its way the light is sorted into its constituent colours by means of a constant deviation prism; the match can therefore be made for any desired colours in succession.

By trial it was found that the most suitable strengths of acid and thio-sulphate to use were such that the first sign of blue *diffracted* light appeared about two minutes after mixing, at ordinary temperatures. The exact strengths used in the present work were 0.051 gm. molecule thiosulphate per litre and 0.106 gm. molecule of HCl per litre. These were approximately chemically equivalent.

It was soon found that, to obtain any concordance in the results obtained on different occasions, it was necessary to pay particular attention to temperature and also to keep the solution continually stirred. Stray light had to be excluded as far as possible, as it seriously affected the power of the eye in matching the two halves of the beam. It was also necessary to guard against fatigue of the eye in the course of an experiment. The rectangular glass cell containing the solution was of 1 cm. internal diameter. This was immersed in a larger one containing water to keep the temperature constant,

* 'Comptes Rendus,' 1906, vol. 143, p. 167.

while between this and the source of light another water cell was placed to act as a heat screen. As source of light a Welsbach mantle was employed. Various heat and light screens were placed where experience indicated. A thermometer was placed in the solution. Air was continually bubbled through to prevent the particles settling and to make their growth as regular as possible. The air tube was arranged so that the stream of bubbles was outside the field of view. A very steady stream of air was obtained from a toy vertical steam engine driven "backwards" by an electric motor. To prevent any considerable evaporation a glass plate was placed over the top of the small cell. The reaction was complete in about 30 minutes. At the close of an experiment the cell was cleaned with a wet plug of cotton wool to remove any adhering sulphur, thoroughly washed out with distilled water, and dried by a stream of dust-free air.

Two typical wave-lengths—one in the blue and the other in the red—were selected, and the complete experiment performed with one wave-length at a time. The final curves obtained (fig. 1) are each composed of three sets of

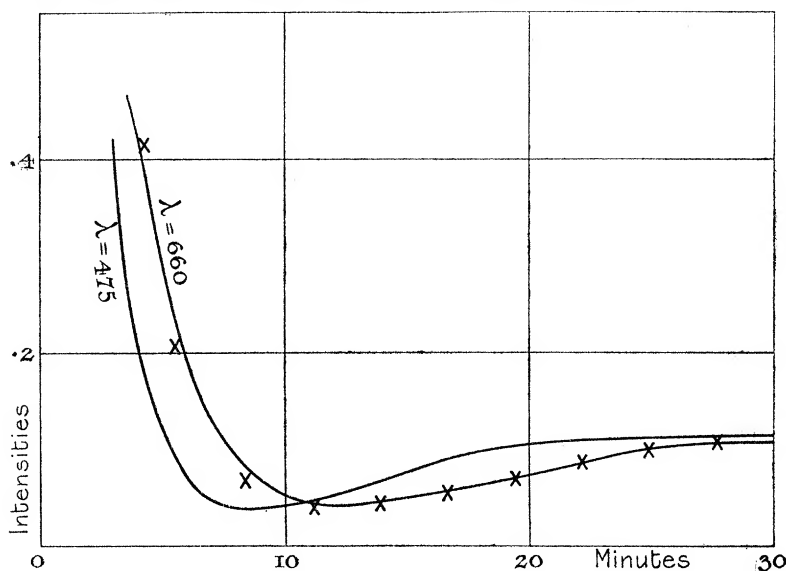


FIG. 1.

readings obtained in this manner. The readings for either wave-length do not differ among themselves by more than the experimental error involved in setting the nicol.* It will be noticed that the initial portion of each curve is not

* The experimental points have been omitted to prevent confusion. The magnitude of the experimental error, however, is slightly less than that between the values indicated by circles in fig. 2 and the mean curve drawn through them.

given. There are two reasons for this omission. In the first place very little of the light is diffracted at this early stage of the reaction, consequently the image of the source is too bright to permit of accurate comparison of the intensity of the two halves of the beam, as considerable movements of the adjustable nicol then produce no appreciable variation of intensity. The second source of error is due to the rapid rate at which the intensity changes in the early stages of the reaction, that is to say, immediately after the first pause during which no deposit is formed. This obviously makes any experimental error of more importance.

Reliable readings of this initial portion of the curve were obtained in separate experiments by interposing a colour screen in the path of that portion of the beam which passes through the solution. Although this reduced the intensity of the light in an ascertainable ratio, it made the accuracy in setting the nicol much greater, as a small movement of the nicol now

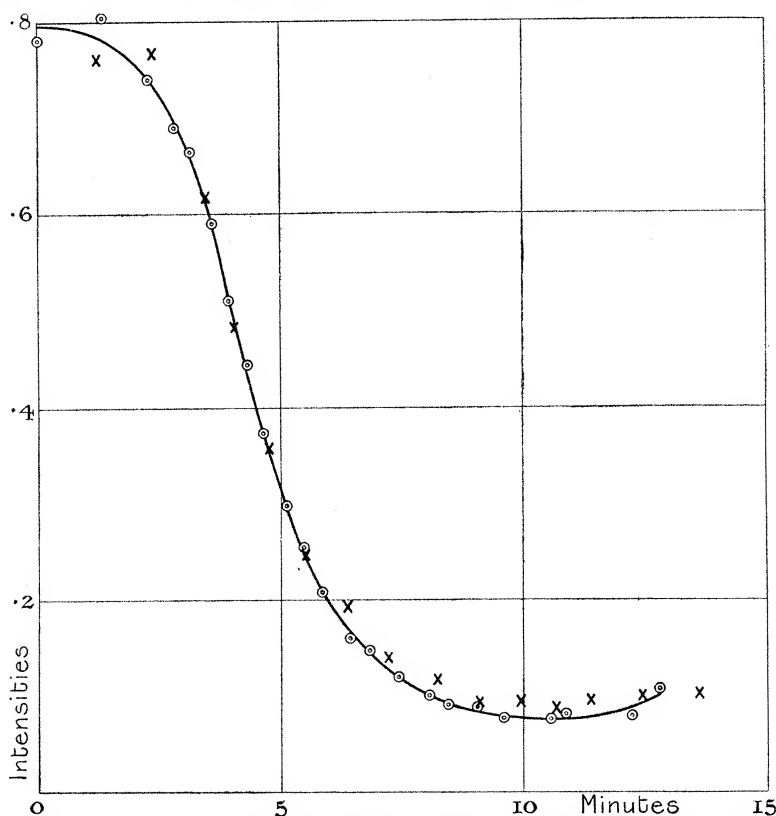


FIG. 2.—Curve showing intensity of transmitted light ($\lambda = 535$) in the early stages of the reaction.

○ with colour screen
 × without colour screen

} Temperature = 14° C.

produced appreciable effect on the intensity. From these readings the corresponding intensities, had the screen been absent, were easily obtained. With the help of an assistant to read the watch, readings were taken at shorter intervals. The curve obtained is shown in fig. 2, the readings being indicated by circles. A control experiment was made without the colour screen; these readings are indicated by crosses.

As already mentioned, the growth of the particles is very sensitive to temperature changes. In fig. 3 are shown two curves to indicate this. The temperatures were adjusted by putting hot water or ice in the water-bath.

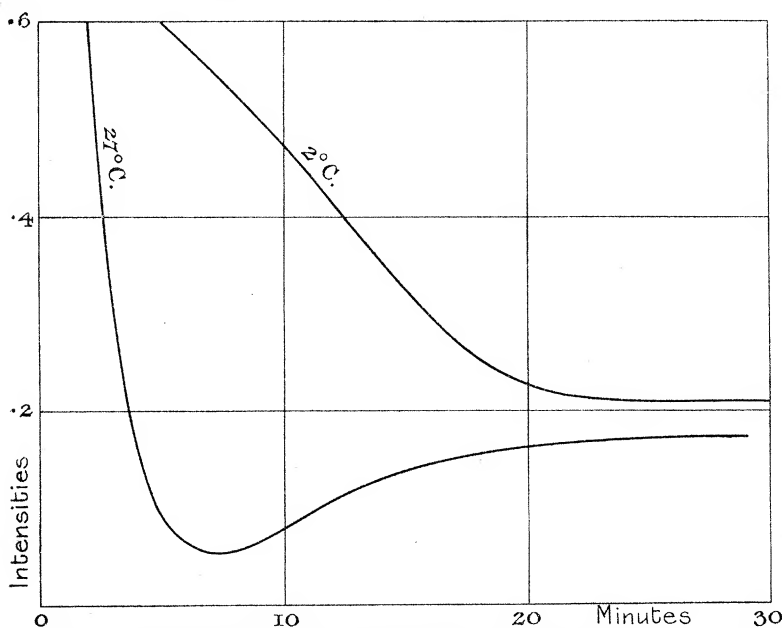


FIG. 3.—Curves showing the effect of temperature upon the reaction. $\lambda = 660$.

Naturally the temperature could not be kept very constant by this means and these curves must be regarded as qualitative only. The character of the curve is very different at the two temperatures, the observations at the lower temperature not indicating the dip which is the subject of this paper. It should be observed that the data for figs. 2 and 3 were taken with a different experimental cell from those for fig. 1.

The size of the particles was measured with the microscope when the intensity of the light passing through was a minimum, *i.e.* about 10 minutes after mixing (see fig. 1). At the end of 10 minutes a drop of the solution was placed on a slide, and further action was then stopped by neutralising the unchanged acid with ammonia. The extreme limits of variation were from 6μ to 10μ , thus indicating that the particles at this stage were considerably

larger than those used by Lord Rayleigh in his experiments.* This was confirmed by repeating his experiments with solutions of the strength mentioned above. Particles of the size used by Lord Rayleigh give rise to the early portion of the curve in fig. 2.

The gradual change of the transmitted light from red through blue to white is well brought out by the curves in fig. 1. In the first stages of the reaction the intensity of the blue light falls off more rapidly than the red. At the end of about 8 minutes the blue light has reached its minimum intensity and begins to increase, while the red light is still falling to its minimum. The transmitted light—when due allowance is made for the rest of the spectrum—becomes a purple colour. After the curves cross, the blue end of the spectrum predominates, and hence we get the blue colour of the transmitted light, which gradually changes to white as the remaining rays increase in intensity. The minimum and final intensities are the same for each wave-length. The final intensity (the horizontal portion of the curves) remains constant for a considerable time and then very slowly increases, owing to the coagulation and consequent settling of the sulphur particles.

Interesting information on the rate of growth of the particles is afforded by an examination of the curves given in fig. 1. If the abscissæ of the curve for blue light are increased in the ratio of the wave-lengths, *i.e.* 660/475, the new points are very nearly coincident with the curve for red light. The points so obtained are indicated by crosses. As one would expect, the agreement is not so complete in the initial portion of the curves, but over the greater part very good agreement holds. This result shows that the transmitted intensity may be represented as a function of t/λ , where t is the time. With regard to the relation between the time and the diameter of the particles more difficulty exists. In the range through which Lord Rayleigh has extended his calculations, the intensity is a function of the diameter divided by λ . This would make the diameter of the particles increase proportionally to the time. Too much uncertainty exists in regard to the physical processes involved during the growth of the particles to devise with any confidence a theoretical value for the rate of growth. We may safely assume a practically instantaneous liberation of thiosulphuric acid, which then decomposes. If this were all, the rate of liberation of sulphur would be proportional to the undecomposed thiosulphuric acid, or

$$dx/dt = K(a-x), \quad \text{and} \quad x = a(1 - e^{-Kt}),$$

so that x itself would be a linear function of t in the early stages. But experimental evidence is in favour of the existence at first of supersaturation,

* 'Collected Papers,' vol. 5, p. 547 ; 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 25.

which at last gives way with a sudden deposition of sulphur particles, which then grow. If we assume that the thiosulphuric acid has decomposed according to the monomolecular law throughout, and that from this stage all that is formed deposits on the particles, the same equation will still hold good for the period after the sudden deposition. But this law is too simple an account, for the process will be mainly controlled by the diffusion of supersaturated solution toward the formed particles. The amount reaching the particles may be taken as proportional to their area or to their (mass)^{2/3}, and the equation becomes

$$dx/dt = Kx^{2/3}(a-x).$$

In the early stages (for which $a-x$ can be treated as constant) this leads to

$$x^{1/3} = \text{const.} \times t,$$

so that the diameter would be a linear function of the time.

In the recent paper by Lord Rayleigh, which we have cited, interesting changes are shown to take place in the polarisation of the light as the particles increase, but there does not appear to be any indication of the phenomena with which this paper deals. We have not found it possible to modify the theoretical equations, so as to make the calculations manageable for the larger particles with which we seem chiefly to be concerned. The phenomena appear to be analogous to the different order spectra obtained with an ordinary grating. The results are published in the hope that the attention of mathematicians may be called to an interesting but very difficult region which still requires mathematical treatment.
